

**THE EFFECT OF POLYMER CONCENTRATION ON THE DEVELOPMENT  
OF POLYSULFONE (PSU) MEMBRANE FOR CARBON DIOXIDE (CO<sub>2</sub>) AND  
METHANE (CH<sub>4</sub>) SEPARATION**

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requirements for the award of the degree of  
Bachelor of Chemical Engineering**

**Faculty of Chemical and Natural Resources Engineering  
University Malaysia Pahang**

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## ABSTRACT

Membrane based gas separation process technology has been recognized as one of the most efficient and advanced unit operation for the gas separation process. The main problem in membrane gas separation is the tradeoff between the permeability and selectivity. The effect of Polysulfone (PSU) polymer concentration was studied to find out the optimum polymer concentration and gives the best performance to the developed membrane. Asymmetric gas separation membranes were prepared from polysulfone (PSU) polymer with three different polymer concentration. Casting solution in this study consisted of polysulfone (PSU) as a polymer, 1-methyl-2-pyrrolidone (NMP) as a solvent while distilled water was used as non solvent additive. The prepared membrane was tested using permeation test unit by using CO<sub>2</sub> and CH<sub>4</sub> as a test gaseous. From the experimental result, the highest selectivity had been achieved at polymer concentration of 32.5% with the selectivity was 2.56 while for the lowest selectivity had been found at polymer concentration of 22% where the selectivity was 1.42. The optimum selectivity was found at pressure 2 bars. The membranes were further characterized by scanning electron microscopy (SEM) to investigate the morphology of membranes respectively. As a conclusion, the polymer concentration parameter is given big effect to the performance of membrane.

## ABSTRAK

Teknologi membran untuk proses pemisahan gas telah diakui sebagai salah satu unit operasi yang paling cepat bagi proses pemisahan gas. Masalah utama dalam pemisahan gas membran adalah tradeoff antara kadar ketelapan dan kememilihan. Pengaruh kepekatan Polisulfon (PSU) polimer dikaji untuk mengetahui kepekatan polimer yang optimum dan memberikan prestasi terbaik kepada membran yang dihasilkan. Membran asimetrik dihasilkan dari polimer polisulfon (PSU) dengan tiga kepekatan polimer yang berbeza. Larutan polimer dalam kajian ini terdiri daripada polisulfon (PSU) sebagai polimer, 1-metyl-2-pyrrolidon (NMP) sebagai pelarut dan air suling. Membran diuji dengan menggunakan unit kebolehtelapan gas dengan carbon dioksida ( $\text{CO}_2$ ) dan methana( $\text{CH}_4$ ) sebagai gas uji. Dari hasil percubaan, kememilihan tertinggi telah dicapai pada kepekatan polimer 32,5% dengan kememilihan 2.56 sedangkan untuk kememilihan terendah telah didapati pada kepekatan polimer 22% iaitu 1.42. Nilai kememilihan optimum telah ditemui pada tekanan 2 Bar. Pencirian struktur membran kemudian dijalankan menggunakan mikroskopi elektron imbasan (SEM) untuk mengkaji struktur dan morfologi membran. Sebagai kesimpulan, parameter kepekatan polimer memberikan pengaruh yang besar terhadap prestasi membran.

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## LIST OF ABBREVIATIONS

A	-	Surface area of the membrane (cm <sup>2</sup> )
AFM	-	Atomic Force Microscopy
CH <sub>4</sub>	-	Methane
CO <sub>2</sub>	-	Carbon dioxide
CV	-	Coagulation Value
GS	-	Gas Separation
i	-	Component i
j	-	Component j
LPG	-	Liquid Petroleum Gas
MF	-	Microfiltration
NG	-	Natural Gas
NMP	-	1-methyl-2-pyrrolidone
P	-	Pressure (bar)
$\Delta p$	-	Transmembrane pressure
PSU	-	Polysulfone
Q	-	Volumetric flow rate (ml/s)
RO	-	Reverse osmosis
S1	-	Polymer solution 1
S2	-	Polymer solution 2
S3	-	Polymer solution 3
SEM	-	Scanning Electron Microscopy
UF	-	Ultrafiltration

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# THE EFFECT OF POLYMER CONCENTRATION ON THE DEVELOPMENT OF POLYSULFONE (PSU) MEMBRANE FOR CO<sub>2</sub> AND CH<sub>4</sub> SEPARATION

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## Abstract

Membrane based gas separation process technology has been recognized as one of the most efficient and advanced unit operation for the gas separation process. The main problem in membrane gas separation is the tradeoff between the permeability and selectivity. The effect of Polysulfone (PSU) polymer concentration was studied to find out the optimum polymer concentration and gives the best performance to the developed membrane. Asymmetric gas separation membranes were prepared from polysulfone (PSU) polymer with three different polymer concentration. Casting solution in this study consisted of polysulfone (PSU) as a polymer, 1-methyl-2-pyrrolidone (NMP) as a solvent while distilled water was used as non solvent additive. The prepared membrane was tested using permeation test unit by using carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) as a test gaseous. From the experimental result, the highest selectivity had been achieved at polymer concentration of 32.5% with the selectivity was 2.56 while for the lowest selectivity had been found at polymer concentration of 22% where the selectivity was 1.42. The optimum selectivity was found at pressure 2 bars. The membranes were further characterized by scanning electron microscopy (SEM) to investigate the structure and morphology of membranes respectively. As a conclusion, the polymer concentration parameter is given big effect to the performance of membrane.

**Keywords:** Polysulfone (PSU), Gas separation, Polymer concentration

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## 1.0 Introduction

Membrane technology is a relatively new method that has been developed in the past few decades, but it has been widely adopted in many industries compared with traditional separation process, such as distillation, extraction and filtration. In general, membrane are thin layers, that can have significantly different structures, but all have the common feature of selective transport to different components in a feed (Naylor, 1996). Commercial applications include carbon dioxide (CO<sub>2</sub>) stripping from natural gas streams, production of high-purity nitrogen from air, and separation of hydrogen from refinery process streams.

Performance of membrane strongly depends on the permeability and selectivity of the membrane. Membrane with higher permeability leads to higher productivity and lower capital costs whereas membrane with higher selectivity leads to higher recovery and lower power cost. In general, membranes that simultaneously possess high values of selectivity and permeability would lead to the most economical separation process. For example, the higher selectivity of a membrane will result to the lower losses of hydrocarbons as CO<sub>2</sub> that being removed and therefore the higher the volume of salable product. CO<sub>2</sub> which falls into the category of

acid gases is commonly found in Natural Gas (NG). CO<sub>2</sub> needs to be removed in order to; increase the heating value of the gas, prevent corrosion of pipeline and process equipments and crystallization during liquefaction process (Bhide and Stern, 1993).

Unfortunately, it is commonly known that polymers which are highly permeable to gases will have low selectivity and vice versa whereas these condition have representing major problem in production and application of commercial separation membranes. Most of membranes selectivity is inversely proportional with permeability (Cailing *et al*, 2007). The most important parameter for tailoring membrane properties which has been identified is polymer concentration (Ahmad, A.L. *et al*, 2005).

From the previous studies of Aroon *et al* (2010), they found that higher selectivity of a membrane can be achieved by increasing the polymer concentration. At the same time, as the polymer concentration in solution is increased, the rejection is also increased while the flux of the membrane will be decreased. As a result, a relatively high percentage of separation is accompanied by a low flux for gas separation; or vice versa.

Therefore, this present study is concentrates on the development and optimization of membrane



formation process due to polymer concentration in order to produce good membrane in both quality and performance for carbon dioxide and methane separation.

## 2.0 Experimental Method

### 2.1 Materials

Polysulfone (PSU) was used as the base polymer for the solution and 1-methyl-2-pyrrolidone (NMP) with purity more than 99.5 % was purchased from Merck was used as solvent without further purification.

### 2.2 Turbidimetric titration test

In order to find the new formulation of dope solution, turbidimetric titration test was applied to identified the exactly amount of NSA which can bring the initial composition of the casting solution nearer to the precipitation point that called cloud point. To measure the cloud point, distilled water was added dropwise in 100g of polymer solution while mixing thoroughly. The addition of water was stopped when the solution became remaining cloudy for some time.

### 2.3 Preparation of asymmetric flat sheet membrane

Membranes were prepared using new ternary dope formulations of casting solutions from the turbidimetric titration test as shown in Table 1. Asymmetric flat sheet Polysulfone membrane were fabricated via dry/wet phase inversion techniques using a stainless steel casting block at an approximately constant shear rate. Water was used as the first coagulation bath to induce the polymer precipitation for 1 day. Subsequently, the membrane was immersed in methanol for another 1 day to ensure the excess solvents were totally removed and to strengthen the molecular structure build in the membrane. The membrane was dried at room temperature for 1 day before use. The membranes were coated using silicone rubber coating to enhance the selectivity since the defects on the surface have been seal smoothly.

### 2.4 Gas permeation using pure CO<sub>2</sub> and CH<sub>4</sub> gaseous.

The gas permeation method involves measurement of a pressure increase with respect to

time due to the accumulation of permeating gases in constant volume under isothermal conditions. Feed pressure was controlled at 1,2,3,4 and 5 bars. Gas permeation rates were measured by soap bubble flow meter. With the data collected, the membrane's gas permeability is calculated.

$$(P/l) = (Q/A \Delta p) \quad (1)$$

Where  $Q$  is volumetric flow rate of the gas,  $\Delta p$  is the pressure difference across the membrane,  $A$  is the membrane effective surface area,  $l$  is the membrane skin thickness and  $P$  is defined as pressure normalized flux for the gas measured. Commonly unit used for pressure normalized flux of a membrane is GPU.

$$1 \text{ GPU} = 1 \times 10^{-6} \text{ cm}^3 (\text{STP}) \text{ cm/cm}^2 \text{ s cmHg} \quad (2)$$

Selectivity of a membrane,  $\alpha$  (unitless) is determined by the ratio of membrane pressure normalized flux in two different gases.

$$\alpha = P_i/P_j = (P/l)_i/(P/l)_j \quad (3)$$

Where  $P_i$  is the pressure normalized flux of a membrane for separation of  $i$  gas and while  $P_j$  is the pressure normalized flux of a membrane for separation of  $j$  gas.

## 2.4 Membrane morphology

The cross section, skin thickness and surface of the fabricated membranes was inspect using Scanning Electron Microscopy (SEM). For this purpose, the membrane samples were fractured in liquid nitrogen and sputtered with platinum, before observation under microscope.

## 3.0 Results and Discussions

### 3.1 Turbidimetric titration for dope formulation

Table 1 shows the result of the turbidity titration test that has been done. The amount of water required to achieve the cloud point is increasing with decreasing in the amount of polymer concentration. It seems that the phase separation may take place in an earlier stage of solvent-non solvent exchange for a higher polymer concentration. However, the higher viscosity of the solution delays the solvent-polymer demixing by slowing down the process of solvent – non solvent exchange. A skin layer is formed before the demixing occurs and the thickness of the skin

layer increases with increasing of polymer concentration (Ismail *et al.*, 2010). It has been generally accepted as a common rule that thermodynamically less stable membrane forming systems can enhance the precipitation rate and make more porous membranes. Thus, in this phase of study all of the three new developed dope solution were design specifically to be thermodynamically less stable system in order to prepare membrane with porous structure.

Table 1 Comparison of dope formulation before and after turbidimetric titration

Before the turbidimetric titration			
Component	Solution Composition (wt. %)		
	S1	S2	S3
Polysulfone (PSU)	25	30	35
1-methyl-2-pyrrolidone(NMP)	75	70	65
After the turbidimetric titration			
Component	Solution Composition (wt. %)		
	S1	S2	S3
Polysulfone (PSU)	22	28	32.5
1-methyl-2-pyrrolidone(NMP)	72.3	66.7	62.5
Distilled water	5.7	5.3	5.0

### 3.2 Effect of polymer concentration on uncoated membrane performance

Table 2 Effect of polymer concentration on uncoated membrane performance

Solution	Polymer Content (wt. %)	Average pressure Normalized Flux(GPU) of CO <sub>2</sub>	Average pressure Normalized Flux(GPU) of CH <sub>4</sub>	Selectivity of CO <sub>2</sub> /CH <sub>4</sub>
S1	22	613.94	490.97	1.25
S2	28	221.18	154.75	1.43
S3	32.5	233.02	134.85	1.73

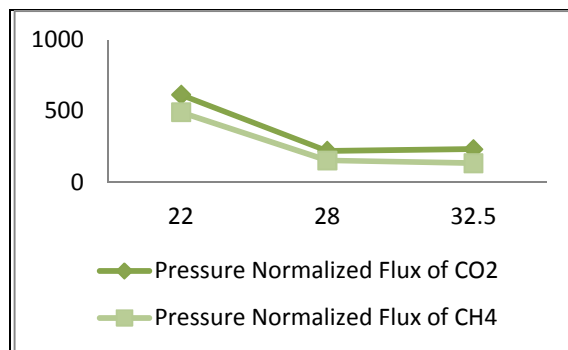


Figure 1. Pressure Normalized Flux of uncoated membranes versus polymer concentration at 2 bars.

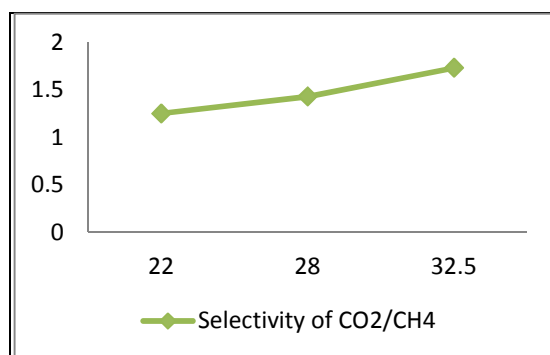


Figure 2. Selectivity of uncoated membranes versus polymer concentration at 2 bars.

The results shows that the pressure normalized flux of the uncoated membranes are high but the selectivity is low. According to Norida, (2004), this is probably due to the skin layer pores (defects) are dominant and the enhancement of free volume in the ultrathin skin layer and the high free volume means better gas permeation (Powell *et al.*, 2006). Abedeni *et al.* (2010) stated that the permeation of gas through porous membrane consists of Knudsen diffusion and Poiseuille flow and the properties of Knudsen to Poiseuille are governed by the ratios of pore radius and the mean free path of the gas molecules. In Knudsen flow, there are more collisions with the pore walls than between gas molecules. At every collision with pore walls, the gas molecules are momentarily absorbed and then reflected in a random direction. As there is less number of collisions among molecules than pore walls, each molecule will move independent of others. Hence, the separation is achieved because gases are moving at different velocities. As a conclusion, the pressure normalized flux will be high and the selectivity will be low.

As shown in the figure 4.2, the highest polymer concentration exhibits the highest value of selectivity among others. The selectivity is 1.73 at 32.5 wt. % of polymer concentration. However, the pressure normalized flux is low. This condition is fit with the theoretical statement that stated the increase of the polymer concentration would increase the membranes selectivity and the pressure normalized flux would be decrease.

### 3.3 Effect of polymer concentration on coated membrane performance

Table 3. Effects of Polymer concentration on coated membrane performance.

Solution	Polymer Content (wt. %)	Average pressure Normalized Flux(GPU) of CO <sub>2</sub>	Average pressure Normalized Flux(GPU) of CH <sub>4</sub>	Selectivity of CO <sub>2</sub> /CH <sub>4</sub>
S1	22	72.20	50.94	1.42
S2	28	56.31	35.69	1.58
S3	32.5	89.94	35.12	2.56

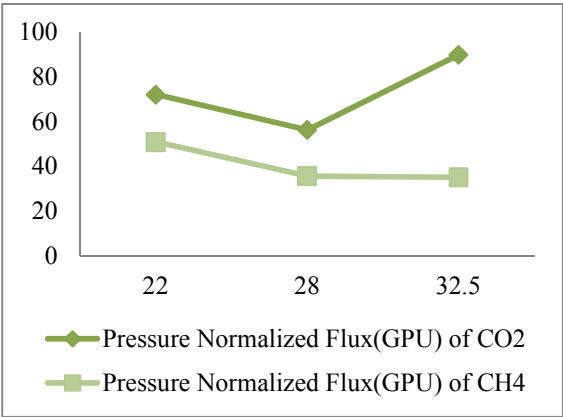


Figure 3. Pressure Normalized Flux of coated membranes versus polymer concentration at 2 bars.

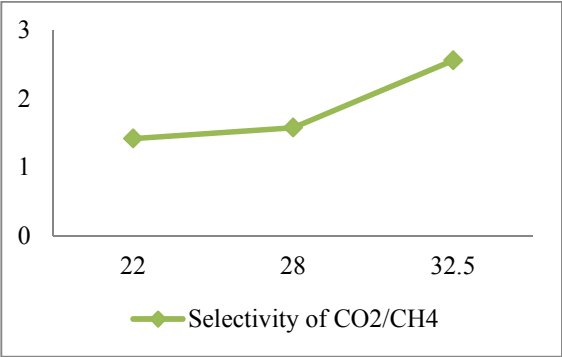


Figure 4. Selectivity of coated membranes versus polymer concentrations at 2 bars.

In order to improve the membrane performance (permeability and selectivity), the membrane surface was coated using 3 w/w % silicone with n-hexane solution. This coating technique will prepare the membranes with composite membrane coating on the membrane surface (for defect free top layer of asymmetric membrane).The advantage of using this coating technique is that it circumvents the difficulty of membrane with a perfect skin (Norida, 2004).The results revealed that the pressure normalized-flux is decrease whereas the selectivity is increases with increasing of polymer concentration on coated membrane. The reason is that the resistance of gas permeance increases with an increase of the thickness of skin layer while the coating solution plays an important role by seal off the defects on the surface layer of the membranes. In the same time, both mean pore size and surface porosity will be decreased. This suggests that increasing polymer concentration will formed a denser and thicker skin layer, resulting in a more selective but less productive asymmetric flat sheet polysulfone membrane for gas separation. On the other hand, membrane prepared from the most dilute polymer solution (Solution S1) produced a thin and porous skin layer, leading to a high value of flux but a relatively low percentage of selectivity. The membrane at polymer concentration of 32.5% exhibited the best performance among the others with pressure normalized flux of CO<sub>2</sub> is 89.94 GPU and the CO<sub>2</sub>/CH<sub>4</sub> selectivity is 2.56. Increasing the polymer concentration of casting solutions causes the solution viscosity to increase ( Ahmad, 2005).The increase in viscosity of polymer solution can delay the diffusional exchange rate of solvent (NMP) and non-solvent (water) in sub-layer, which makes the precipitation rate of sub-layer become slower (Kim and Lee, 1998). As a result of fast phase separation at outer skin layer and slow phase separation at sub-layer, the asymmetric membrane having a dense and

thick skin layer supported by a closed cell sub-layer was produced. In contrast, asymmetric membrane with a thin and porous skin layer and open cell sub-layer was prepared by polymer solutions consisting of lower polymer concentration.

3.2 Effect of feed pressure on coated and uncoated membrane performance.

The pressure normalized flux and selectivity of the coated and uncoated membranes for each polymer concentration were determined as a function of feed pressure. The measurements were carried out at room temperature and pressures 1 to 5 bars. The effect of feed pressure on the membranes performance for coated and uncoated membranes were shown in the following figures; Figure 5 to Figure 10.

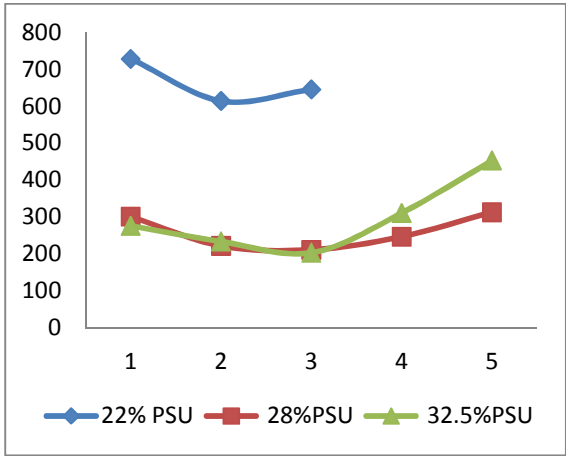


Figure 5. Average Pressure Normalized flux (GPU) of CO<sub>2</sub> versus pressure (bars) for uncoated membrane

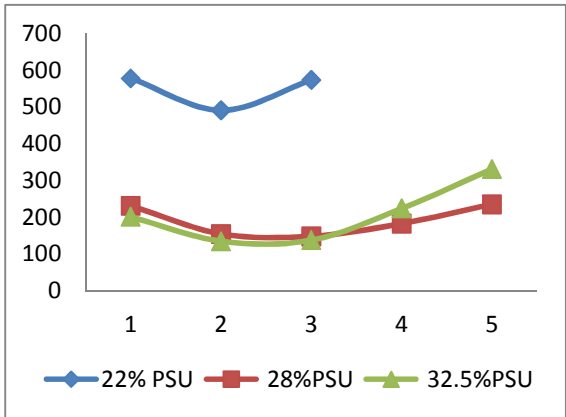


Figure 6. Average Pressure Normalized flux (GPU) of CH<sub>4</sub> versus pressure (bars) for uncoated membranes

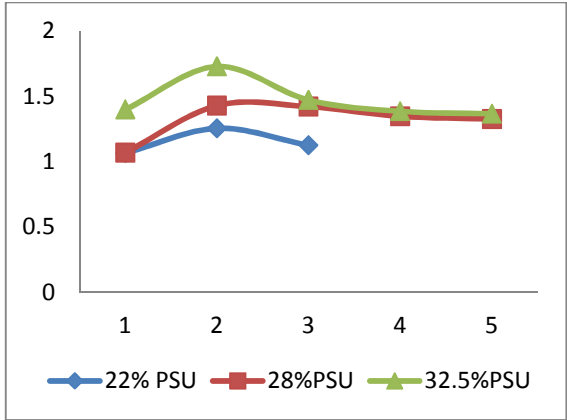


Figure 7. Average Selectivity of CO<sub>2</sub>/CH<sub>4</sub> versus pressure (bars) for uncoated membranes

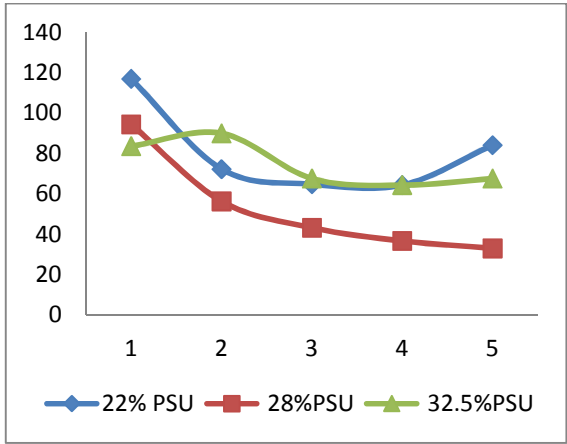


Figure 8. Average Pressure Normalized flux (GPU) of CO<sub>2</sub> versus pressure (bars) for coated membranes

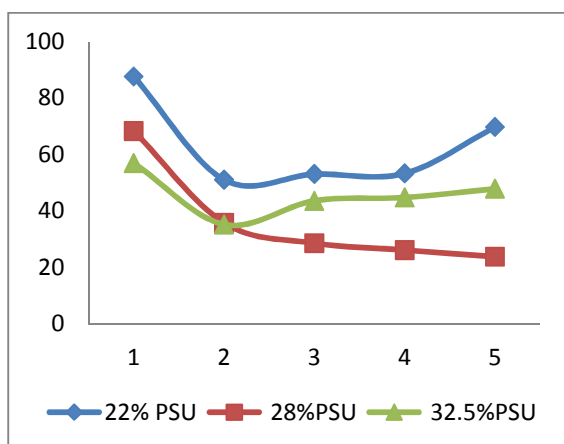


Figure 9. Average Pressure Normalized flux (GPU) of CH<sub>4</sub> versus pressure (bars) for coated membranes

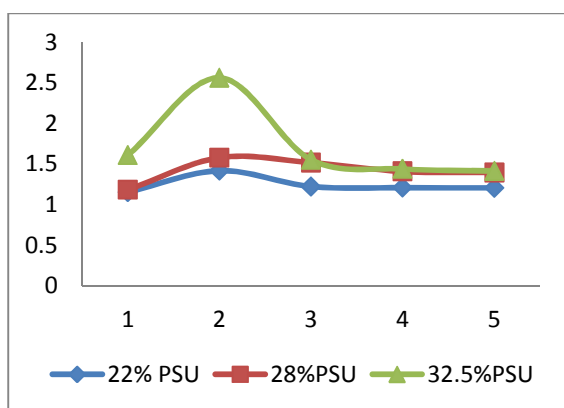


Figure 10. Average Selectivity of CO<sub>2</sub>/CH<sub>4</sub> versus pressure (bars) for coated membranes

Change in the pressure applied on the membranes may cause large variations on the membranes performance. Koros and Chern (1987) stated that a decreasing trend of permeability with increasing pressure was typically observed with highly soluble gases such as CO<sub>2</sub> in glassy polymers. On the same time, the increase in feed pressure improves the selectivity of the membrane (Ismail, 2009). It is due to the fact that the increased pressure creates a greater driving force across the membrane. However, the maximum pressure that achieved for the best selectivity on the coated and uncoated membranes was found at 2 bars. This suggests that when the feed pressure was increased to 3 bars and above, the pore size become smaller due to the high concentration of the feed gas. As a result, the selectivity was decreased at feed pressure 3 to 5 bars.

### 3.3 Morphology and characterization for coated and uncoated membrane

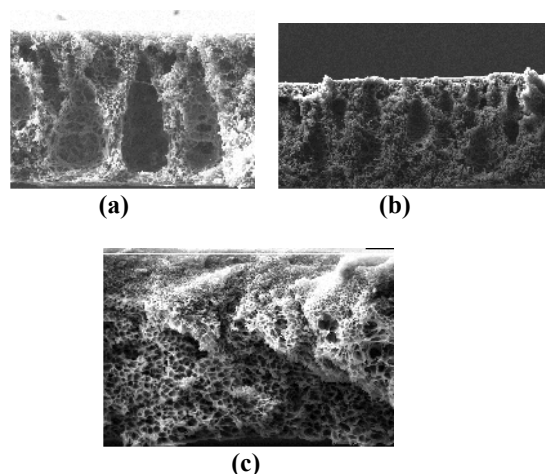


Figure 11. The cross-section of uncoated flat sheet Polysulfone (PSU) membranes: (a) for solution S1, (b) for solution S2, (c) for solution S3.

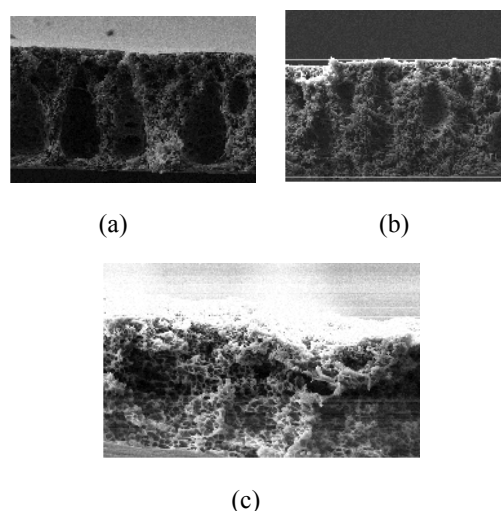


Figure 12. The cross-section of coated flat sheet Polysulfone (PSU) membranes: (a) for solution S1, (b) for solution S2, (c) for solution S3.

As seen in Figure 11 (a)-(c) and Figure 12 (a)-(c), there are no significant different in the cross sectional structure of the coated and uncoated membrane. This is due to the fact that membrane coating technique will be prepared the membrane with composite surface layer whereas the nascent in the membrane structure was happened during the dry/wet phase separation process. All the fabricated membranes display asymmetric structures with a combination of skin layer and supporting layers. Both layers have significant role in membrane transport



properties. S1 membrane comprises a skin layer that was well-developed and supported by a porous support layer with large finger-like, sponge-like and macrovoid structures.

This is due to solvent -non- solvent exchange, leading to the different starting conditions for phase separation at layers far from the surface and the formation of macrovoids is happened when non-solvent diffusion rate into the polymer-poor phase being formed exceeds the rate of outward-solvent diffusion (Sofiah *et al.*, 2010). This signifies that an increase macrovoids formation in S1 membrane was due to its lower polymer concentration used in the dope preparation. Solution S2 membrane shows that the finger-like pores decrease in size and number while the support layer in the lower part of the membrane was increased. Solution S3 presents the densest skin layer compared to the other fabricated membranes with the other polymer concentration. It displayed tiny and micropore finger-like structure resulting from the high percentage of polymer concentration which enhanced the viscosity of the dope solution, leading to the formation of smaller pore size.

This phenomenon occurs since high viscosity would avoid the diffusion exchange rate of solvent and non-solvent in sub-layer inducing fast-phase separation at the skin layer hence slowing the precipitation rate of the sub-layer (Sofiah *et al.*, 2010). This results in the formation of an asymmetric membrane with dense and thick skin layer supported by a closed cell sub-layer. Besides, higher polymer concentration induced the chain entanglement and therefore reduced the formation of the macrovoid in the skin layer. On top of that, these conditions were affected by the thicker selective skins and transition layers which resulted from the slower redissolution of initial phase outermost separated regions of nascent membranes from an underlying homogeneous solution during dry-phase separation (Ahmad *et al.*, 2005).

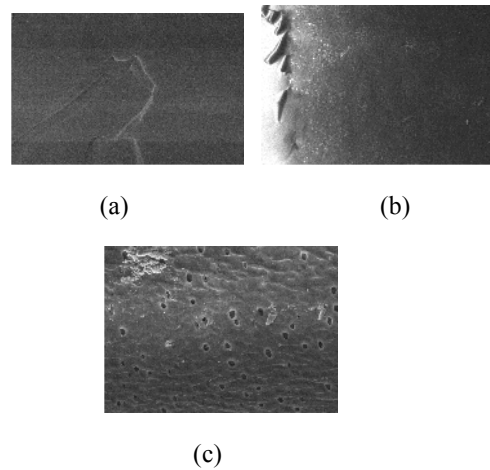


Figure 7 Surface layer structure of uncoated flat sheet Polysulfone (PSU) membrane, (a) for solution S1, (b) for solution S2, (c) for solution S3.

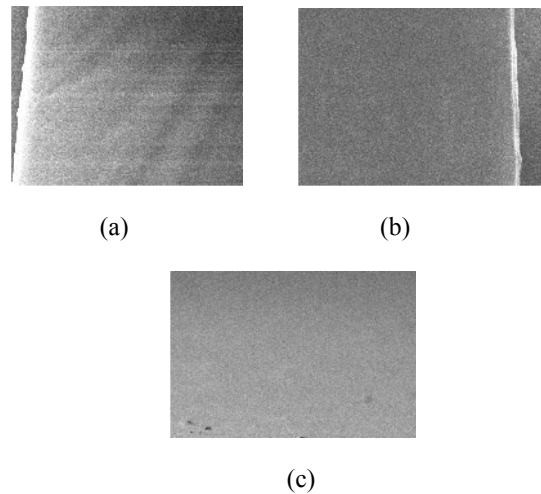


Figure 8 Surface layer structure of coated flat sheet Polysulfone (PSU) membrane, (a) for solution S1, (b) for solution S2, (c) for solution S3.

Figure 7 (a-c) and Figure 8 (a-c) shows the comparison of the membrane surface layer structure when coated and uncoated with silicone rubber coating. From the figure, it shows that surface layer of coated membrane is smoother than uncoated membrane. There are no defects that can be found on the coated membrane surface layer. From the membrane performance, membrane with silicone rubber coating was able to enhance higher selectivity since the defects on the surface have been seal smoothly and the free volume in the ultrathin skin layer is decreased. As a result, low performance of gas permeation is accompanied by high selectivity due to the formation of an asymmetric membrane with dense and thick composite skin layer.

#### 4.0 Conclusion

Based on the results of this study, a number of conclusions were drawn.

1. The highest selectivity of uncoated membrane for CO<sub>2</sub> and CH<sub>4</sub> separation was found at the highest polymer concentration solution of 32.5% while the lowest polymer concentration solution; 22% exhibited the lowest selectivity. Same phenomena was found for coated membranes where the highest selectivity of uncoated membrane for CO<sub>2</sub> and CH<sub>4</sub> separation was found at the highest polymer concentration solution of 32.5% while the lowest polymer concentration solution; 22% exhibited the lowest selectivity.
2. Increasing polymer concentration of dope solution increases skin thickness but decreases surface porosity (denser skin) of asymmetric flat sheet Polysulfone (PSU) membrane. As a result, a relatively high percentage of separation is accompanied by a low flux for gas separation; or vice versa.
3. The performance of coated membrane in term of selectivity is higher than uncoated membrane. This is because the surface pinholes or defect on the membrane surface have been seal with the coating solution. Hence, the free volume on the ultrathin skin was decreased and resulting in better permeability but low selectivity of a membrane performance.
4. All of the membranes display asymmetric structures with a combination of skin layer and supporting layers. Scanning electron microscopy (SEM) shows by increased the polymer concentration in the dope solution results in decreasing of finger-like pores. Hence, densest skin layer was present by the highest polymer concentration solution; 32.5% compared to the other membranes. There are no significant different in the structure of coated and uncoated membrane except for the surface layer. The surface looked smoothly on coated membrane resultant on good performance of coated membranes compared than uncoated membrane.

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